

REMARKS

Claims 1-17 are pending in the application. Claims 18-33 were previously cancelled. No claims have been amended in this reply.

In view of the following remarks, reconsideration and withdrawal of the rejections to the application in the Office Action are respectfully requested.

I. Rejection of Claims under 35 U.S.C. § 103(a) over Wagner in view of Hubbell and Schössler.

Claims 1-8, 13 and 14 remain rejected under 35 U.S.C. § 103(a) as unpatentable over U.S. Patent Application Publication No. 2002/0110932, issued to Wagner *et al.* (hereinafter “Wagner”) in view of U.S. Patent Application Publication No. 2002/0128234, issued to Hubbell *et al.* (hereinafter “Hubbell”) and further in view of U.S. Patent No. 4,822,681, issued to Schössler *et al.* (hereinafter “Schössler”). Applicants respectfully traverse.

Neither Wagner nor Hubbell teaches reactions between gas-phase epoxy-functional molecules and surface hydroxyl groups. The Examiner attempts to overcome the shortcomings in the teachings of Wagner and Hubbell by pointing out that Schössler teaches the reaction of glycidoxypolytriethoxysilane with the hydroxyl groups on a hydroxyl group-containing surface and further teaches that “It is particularly advantageous to effect the activation in gaseous phase through employment of aerosols or by means of underpressure.” However, Schössler does not teach a method of treating a surface of a substrate that includes the step of “reacting *epoxy groups* on gas-phase epoxy-functional molecules with the surface hydroxyl groups *in situ* in the absence of plasma to provide epoxy-terminated surface-bound spacer chains,” as recited in amended claim 1. Rather, Schössler teaches a method that includes the step of reacting silico-functional groups on silico-functional molecules with surface hydroxyl groups on synthetic polymers. (See col. 3, line 68 through col. 4, line 8.) Although the silico-functional molecules may also include epoxy functionalities, as in the case of glycidoxypolytriethoxysilane, these epoxy functionalities are not reacted with the hydroxyl groups on the polymer surfaces in the gas phase reactions of Schössler. Thus, at best, Schössler teaches the possibility of a gas-phase

reaction between silico-groups on gas-phase organosilane molecules and hydroxyl groups on a polymer surface. As such, this teaching provides one of ordinary skill in the art with no information, teaching or suggestion regarding the desirability, or even the possibility, of carrying out gas-phase reactions between *epoxy groups* on epoxy-functional gas-phase molecules and surface hydroxyl groups.

The Examiner takes the position that:

“... one of ordinary skill in the art at the time of the invention would have been motivated to include in the method of Wagner et al. a spacer molecule X-R-Y, wherein X is an epoxy functional group as taught by Hubbell et al., in order to bind the spacer molecule to the hydroxyl groups of the substrate surface of Wagner et al. with a reasonable expectation of success since Wagner et al. teaches that the X group may be chosen as any group which affords chemisorption or physisorption of the monolayer onto the surface of the substrate. ... Moreover, it would have been obvious to one having ordinary skill in the art at the time of the invention to select an appropriate functional group (X and Y) of the spacer molecules X-R-Y, since it has been held to be within the general skill of a worker in the art to select a known material on the basis of its suitability for the intended use as a matter of obvious design choice.” (Office Action, page 7, first full paragraph.)

Applicants respectfully submit that the Examiner's reasoning, as quoted above, misses the point. The question is not whether it would be an obvious design choice to select an epoxy group as the X functionality that reacts with a surface-bound hydroxyl group. Rather, the question is whether it would be an obvious design choice to carry out the reaction between the epoxy group of an epoxy-functional molecule and a surface-bound hydroxyl group *in the gas phase* when all of the relevant prior art teaches only the reaction of epoxy groups with hydroxyl groups *in solution*. It is not an obvious design choice.

With regard to the latter question, the Examiner states:

“... it would have been obvious to one of ordinary skill in the art at the time of the invention to employ a method of reacting a gas comprising spacer molecules

with epoxy functional groups with the surface hydroxyl groups of Wagner et al. in view of Hubbell et al. and Schössler et al. in situ in the absence of plasma since Schössler et al. teaches that activation in gaseous phase through employment of aerosols or by means of underpressure provides an activation technique, which has lower expenditure compared to other activation techniques.” (Office Action, page 8.)

In making this statement the Examiner appears to assume that one of ordinary skill in the art would recognize gas-phase reactions between epoxy groups and hydroxyl groups as known equivalents. One of ordinary skill in the art would recognize no such thing for at least two reasons. First, Schössler actually teaches that epoxy groups on gas phase epoxy-functional molecules do not react with surface hydroxyl groups. Second, one of ordinary skill in the art at the time of the invention would recognize that the solution-phase-reaction mechanism for epoxy and hydroxyl groups taught in each of the prior art references could not work in the gas phase. Each of these two reasons is discussed in detail separately below.

- (A) Schössler teaches that epoxy groups on gas phase epoxy-functional molecules **do not** react with surface hydroxyl groups, thereby **teaching away** from the claimed invention.

As described in the response filed on August 10, 2007, Applicants are aware of no prior art describing a reaction between an epoxy group on *gas-phase* epichlorohydrin molecule and a hydroxy group immobilized on and bound to an inorganic oxide surface. Schössler fails to provide such prior art because Schössler is directed solely to gas phase reactions between *silico* groups on organosilanes and surface hydroxy groups. In fact, the epoxy groups of the gas phase organosilanes of Schössler **do not** react with the surface hydroxyl groups. As acknowledged by the Examiner, these gas phase epoxy groups remain free to react with biological molecules to bind them with the solid body surface. (Office Action, page 6, 3rd full paragraph.) Therefore, to the extent that Schössler is relevant at all, it actually teaches that gas phase epoxy functional groups do not react with surface hydroxyl groups – thereby *teaching away* from a method of treating a surface that includes the step of reacting epoxy groups on gas-phase epoxy-functional molecules with surface hydroxyl to provide epoxy-terminated, surface-bound spacer chains, as

recited in rejected claim 1. For this reason, the combination of Wagner, Hubbell and Schössler fails to render the subject matter of claims 1-8, 13 and 14 obvious and Applicants request that the rejection of these claims be withdrawn.

- (B) The solution-phase-reaction mechanism for reactions between epoxy and hydroxyl groups taught in each of the prior art references could not work in the gas phase and, therefore, the substitution of a gas phase reaction for a solution-phase reaction is not an obvious design choice.

To the extent that the Examiner would like to rely on the teachings of Wagner and/or Hubbell to provide the motivation to carry out a reaction between the epoxy group of an epoxy-functional gas phase molecule and a surface hydroxyl group, Applicants note that both Wagner and Hubbell describe solution-phase chemical reactions. As pointed out in Applicants' previous response, these solution-phase reaction mechanisms cannot take place in the gas phase. For example, the solution-phase reaction between epichlorohydrin and hydroxyl groups involves a ring-opening addition of epichlorohydrin to a hydroxy group in the presence of an acid or alkaline catalyst, followed by a ring-closing reaction via dehydrohalogenation in an alkaline environment. In solution, the presence of water facilitates the reaction by solvating charged species. As evidence of this common knowledge in the art, Applicants enclose herewith two references. The first reference, PCT application publication number WO 96/24628, includes a discussion of the solution-phase reaction between the epoxide group of epichlorohydrin and hydroxyl groups on polyhydric phenols. According to this reference, the reaction "is generally a process wherein a lower molecular weight epoxy is prepared initially by reacting a polyhydric phenol with epichlorohydrin and alkali metal hydroxide in the presence of a catalyst to produce polyeпоxide." (Page 1, lines 21-24; emphasis added.) The second reference, pages 778-779 of the textbook Organic Chemistry, by A.S. Wingrove et al, Harper and Row (1981) illustrates more generally the solution phase reaction mechanisms for reactions between hydroxyl groups and epoxy groups. As shown in sections A.2 and B.2 of these pages the solution phase reaction between an epoxy group and a hydroxyl group (e.g., on water, an alcohol or a phenol) utilizes either an acidic reagent (H^+), a metal catalyst, a basic reagent (OH^-), solvating water molecules, or a combination thereof. Thus, both of the enclosed references illustrate the need for an alkaline

or acid catalyst, a metal and/or water to promote the solution-phase reaction of epoxy functionalities with hydroxyl groups. As one of ordinary skill in the art would certainly recognize, there is no acid catalyst, alkaline catalyst, metals or aqueous environment in the gas phase to facilitate a reaction mechanism analogous to the well known solution-phase reaction mechanisms. Therefore, one of ordinary skill in the art would have no reason to expect that the reaction between an epoxy-functional molecule, such as epichlorohydrin, and a hydroxyl group could be carried out successfully in the gas phase. In fact, in view of Schössler's teaching that gas phase epoxy-functional groups on glycidoxypolytriethoxysilane *do not* react with surface hydroxyl groups, it seems reasonable to conclude that one of ordinary skill in the art would expect the epoxy groups of gas phase epoxy-functional molecules to be unreactive toward surface-bound hydroxyl groups. For this additional reason, the combination of Wagner, Hubbell and Schössler fails to render the subject matter of claims 1-8, 13 and 14 obvious and Applicants request that the rejection of these claims be withdrawn.

II. Rejection of Claims under 35 U.S.C. § 103(a) over Wagner in view of Hubbell, Schössler and Laibinis.

Claims 9 and 10 were rejected under 35 U.S.C. § 103(a) as unpatentable over Wagner in view of Hubbell, Schössler and P.C.T. Patent Application Publication No. WO 01/83826, issued to Laibinis *et al.* (hereinafter "Laibinis"). Applicants respectfully traverse.

Claims 9-10 each depend from claim 1. Claim 1 is patentable over the combination of Wagner, Hubbell and Schössler for the reasons discussed in Section I, above. Like Wagner, Hubbell and Schössler, Laibinis provides one of ordinary skill in the art with no information, teaching or suggestion regarding the desirability, or even the possibility, of carrying out gas-phase reactions between *epoxy groups* on epoxy-functional *gas-phase* molecules and surface hydroxyl groups, and certainly fails to suggest the desirability or feasibility of carrying out a reaction between a *gas-phase* epichlorohydrin molecule and a surface hydroxyl group.

Laibinis' disclosure of reactions between epichlorohydrin and hydroxy groups is limited to the following statement: "In another embodiment, the glass surface is modified with hydroxyl

groups using reagents such as hydroxypropyltriethoxysilane. Subsequent reaction of the hydroxy moiety with epichlorohydrin provides a surface having attached epoxide functional groups.” (Page 19, lines 13-15.) Thus, Laibinis describes a method wherein a hydroxy-functional layer of an organosilane is provided on a glass surface, and this organosilane is subsequently reacted with epichlorohydrin.

Laibinis provides no explanation of how the “subsequent reaction of the hydroxy moiety with epichlorohydrin” would be conducted. In the absence of any prior art teaching of gas-phase reactions between epichlorohydrin and surface hydroxy groups, one of ordinary skill in the art would naturally employ conventional solution-phase methods to carry out the reaction suggested by Laibinis. As discussed in Section I.B, above, these methods generally involve a ring-opening addition of epichlorohydrin to a hydroxy group in the presence of an acid or alkaline catalyst, followed by a ring-closing reaction via dehydrohalogenation in an alkaline environment. Therefore, the combination of Laibinis with Wagner, Hubbell and Schössler fails to render obvious a reaction between an epoxy group on a gas-phase epichlorohydrin molecule and a surface-bound hydroxyl group for at least the two reasons discussed in Section I, above, namely: (1) Laibinis, Wagner and Hubbell describe only solution-phase reactions having reaction mechanisms that could not occur in the gas phase; and (2) Schössler not only fails to teach a reaction between an epoxy group on a gas-phase epoxy-functional molecule and a surface hydroxyl, but suggests that such a reaction does not occur. Therefore, Applicants request that the rejection of claims 9 and 10 be withdrawn.

III. Rejection of Claims under 35 U.S.C. § 103(a) over Wagner in view of Hubbell, Schössler and Devoe.

Claims 11 and 12 were rejected under 35 U.S.C. § 103(a) as unpatentable over Wagner in view of Hubbell, Schössler and P.C.T. Patent Application Publication No. WO 01/96452, filed by Devoe *et al.* (hereinafter “Devoe”). Applicants respectfully traverse.

Claims 11 and 12 each depend from claim 1. As discussed in Section I, above, Claim 1 is patentable over the combination of Wagner, Hubbell and Schössler because the combined

teachings of Wagner, Hubbell and Schössler fail to suggest the desirability or even feasibility of carrying out gas-phase reactions between *epoxy groups* on epoxy-functional, gas-phase molecules and surface hydroxyl groups. It follows that the combined teachings of these references also fail to suggest the desirability or feasibility of carrying out a reaction between a *gas-phase diepoxide* molecule and a surface hydroxyl group. Devoe fails to cure this deficiency.

In support of the rejection of claims 11 and 12, the Examiner states: “Devoe *et al.* teaches that numerous commercially available epoxy resins including 1,4-butanediol diglycidyl ether can be used on a solid surface (Abstract and p. 13, line 12). Therefore, it would have been an obvious matter of design choice to modify Wagner *et al.* in view of Hubbell *et al.* and Schössler *et al.* to include 1,4-butanediol diglycidyl ether of Devoe *et al.* as epoxy-functional molecules ...”

Even assuming (strictly for the sake of argument) that the Examiner’s contention is correct, the teachings of Devoe would not make it an obvious matter of design choice to modify Wagner in view of Hubbell and Schössler to react *gas-phase* 1,4-butanediol diglycidyl ether molecules with surface-bound hydroxy groups. Devoe does not contemplate gas-phase reactions between 1,4-butanediol diglycidyl ether and a surface. Instead, Devoe provides the following description of the application of compositions containing epoxy resins to surfaces: “The compositions may be applied by coating methods such as knife, bar, reverse roll, and knurled roll coating, or by application methods such as dipping, immersion, spraying, brushing, curtain coating and the like. Alternatively, the compositions can be applied drop-wise.” (Page 37, lines 25-28.) Each of these coating methods applies to epoxy resins in a liquid state. Therefore, the combination of Devoe with Wagner, Hubbell and Schössler fails to render obvious a reaction between an epoxy group on a gas-phase diepoxide molecule and a surface-bound hydroxyl group for at least the two reasons discussed in Section I, above, namely: (1) Devoe, Wagner and Hubbell describe only solution-phase reactions having reaction mechanisms that could not occur in the gas phase; and (2) Schössler not only fails to teach a reaction between an epoxy group on a gas-phase epoxy-functional molecule and a surface hydroxyl, but suggests that such a reaction

does not occur. Therefore, Applicants request that the rejection of claim 11 and 12 be withdrawn.

IV. Rejection of Claims under 35 U.S.C. § 103(a) over Wagner in view of Hubbell, Schössler and Dang.

Claims 15-17 were rejected under 35 U.S.C. § 103(a) as unpatentable over Wagner in view of Hubbell, Schössler and U.S. Patent Application Publication No. 2002/0113478, issued to Dang *et al.* (hereinafter “Dang”). Applicants respectfully traverse.

Claims 15-17 each depend from claim 1. As discussed in Section I, above, Claim 1 is patentable over the combination of Wagner, Hubbell and Schössler because the combined teachings of Wagner, Hubbell and Schössler fail to suggest the desirability or even feasibility of carrying out *gas-phase* reactions between *epoxy groups* on epoxy-functional, *gas-phase* molecules and surface hydroxyl groups. Dang fails to cure this deficiency.

The Examiner has failed to identify, and Applicants were unable to locate, any teaching in Dang regarding: (1) reactions between epoxy groups on gas-phase, epoxy-functional molecules and surface-bound hydroxy groups; or (2) reactions between *gas-phase* spacer molecules with epoxy-terminated, surface-bound spacer chains. Therefore, the teachings of Dang fail to remedy the shortcomings of the combined teachings of Wagner, Hubbell and Schössler, and Applicants respectfully request that the rejection of claims 15-17 be withdrawn.

V. Provisional Obviousness-Type Double Patenting Rejections

The Office Action provisionally rejects each of claims 1 and 4-12 under the judicially created doctrine of obviousness-type double patenting, alleging that these claims are unpatentably obvious over certain claims in of co-pending U.S. Patent Application No. 11/690,045.

In view of the foregoing arguments, the only rejections that should remain in the present application are the provisional double patenting obviousness-type rejections based on co-pending U.S. Patent Application No. 11/609,045. Section 804(I)(B) of the M.P.E.P. states,

The “provisional” double patenting rejection should continue to be made by the examiner in each application as long as there are conflicting claims in more than one application unless that “provisional” double patenting rejection is the only rejection remaining in one of the applications. If the “provisional” double patenting rejection in one application is the only rejection remaining in that application, the examiner should then withdraw that rejection and permit the application to issue as a patent, thereby converting the “provisional” double patenting rejection the other applications(s) into a double patenting rejection at the time the one application issues as a patent. (Emphasis added)

Applicants respectfully submit that § 804(I)(B) is applicable, and Applicants respectfully request that the Examiner withdraw the provisional double patenting obviousness-type rejection based on U.S. Patent Application No. 11/609,045 in the present application and allow this application to issue. Applicants specifically reserve the right to challenge the propriety of the double patenting rejection in this application and in U.S. Patent Application No. 11/609,045 as an alternative to filing a Terminal Disclaimer therein.

The Commissioner is hereby authorized to charge any additional fees which may be required regarding this application under 37 C.F.R. §§ 1.16-1.17, or credit any overpayment, to Deposit Account No. 19-0741. Should no proper payment be enclosed herewith, as by a credit card payment being in the wrong amount, post-dated, otherwise improper or informal or even entirely missing, the Commissioner is authorized to charge the unpaid amount to Deposit Account No. 19-0741.

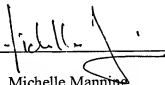
In view of the foregoing remarks, Applicants respectfully submit that all of the claims remaining in the Application are in condition for allowance, and favorable action thereon is respectfully requested. The Examiner is invited to contact the undersigned by telephone if it is felt that a telephone interview would advance the prosecution of the present application.

Respectfully submitted,

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(21) International Application Number: PCT/US95/01674 (22) International Filing Date: 10 February 1995 (10.02.95) (71) Applicants (for all designated States except US): DOW DEUTSCHLAND INC. [DE/DE]; Zweigniederlassung, Stade, Buetzfliebersand, P.O. Box 1120, D-21677 Stade (DE). THE DOW CHEMICAL COMPANY [US/US]; 2030 Dow Center, Abbott Road, Midland, MI 48640 (US). (72) Inventors; and (73) Inventors/Applicants (for US only): RAVENSCROFT, Michael, David [GB/FR]; 3, square de l'Hermine, F-67240 Bischwiller (FR). HOFFMANN, Klaus, Erich [DE/DE]; Kolpingstrasse 24, D-77815 Buehl (DE). GLASS, Terry, Wayne [US/US]; 409 Oyster Creek Court, Richwood, TX 77531 (US). KEILLOR, Peter, Thompson, III [US/US]; 921 Oleander Street, Lake Jackson, TX 77566 (US). POINCLOUX, Jacques, Louis [FR/US]; 69 Bachelor Button, Lake Jackson, TX 77566 (US). ELMS, William, Jay [US/US]; 318 Live Oak Lane, Lake Jackson, TX 77566 (US). (74) Agent: MAURER, Charles, M.; The Dow Chemical Company, Patent Dept., P.O. Box 1967, Midland, MI 48641-1967 (US).		(81) Designated States: AU, CN, CZ, FI, JP, KR, MX, RU, US, European patent (AT, BE, CH, DE, DK, ES, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE). Published <i>With international search report.</i> <i>With amended claims.</i>
(54) Title: EPOXY RESIN COMPOSITION CAPABLE OF CURE AT LOW TEMPERATURE		
(57) Abstract An epoxy resin which is a reaction product of a polyepoxy and a polyol which contains both epoxy groups and terminal phenolic hydroxyl groups of at least 0.2 weight percent having added thereto an epoxy novolac having an epoxy functionality greater than two. The epoxy resin is suitable for use as a powder coating exhibiting lower melt viscosity than prior art resins of similar composition. The epoxy resin exhibits higher T _g /softening point than prior art resins of similar viscosity. A powder coating prepared from the resin may be used on temperature sensitive substrates.		

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EPOXY RESIN COMPOSITION CAPABLE OF CURE AT LOW TEMPERATURE

The present invention relates to epoxy resins, to a process for preparing epoxy resins and to compositions containing epoxy resins.

- 5 Due to their physical and chemical properties such as resistance to chemical attack, good adhesion to various substrates, solvent resistance and hardness, epoxy resins are useful in a wide variety of commercial applications including the coating of various substrates such as metal, and the preparation of structural and electrical laminates. In many applications, such as the coating of the interior of containers ("cans"), the epoxy resin is applied from an
10 organic liquid solution or aqueous dispersions. Powder coatings, which eliminate the need for solvents, are also prepared from epoxy resins.

- The molecular weight of the epoxy resin generally affects the physical properties of the resin, for example: softening point, melt viscosity and solution viscosity of the epoxy resin as well as the physical and chemical properties of the cured product prepared therefrom.
15 A higher molecular weight epoxy resin is generally correlated with increased toughness.

- High molecular weight resins are the reaction product of a polyepoxide such as the diglycidylether of bisphenol A with a polyhydric phenol such as bisphenol A (so-called "advanced epoxy resins"). The advancement reaction occurs between the epoxide group and the hydroxyl of the phenol forming a β -hydroxyl group thereby extending the chain of the
20 molecules. Cross-linking is incidental to the advancement reaction.

- The process of advancement of an epoxy resin is generally a process wherein a lower molecular weight epoxy resin is prepared initially by reacting a polyhydric phenol with epichlorohydrin and alkali metal hydroxide in the presence of a catalyst to produce a polyepoxide. Thereafter, the initial polyepoxide reaction product is advanced by its reaction
25 with additional amounts of polyhydric phenol to form the higher molecular weight material. In conventional techniques for preparing the epoxy resins, the reaction of the polyepoxide and polyhydric phenol is typically carried to complete conversion such that the final, advanced epoxy resin contains relatively low amounts of residual phenolic hydroxyl groups. For example, epoxy resins having an EEW (epoxy equivalent weight) between 500 and 700 prepared from
30 bisphenol A and the diglycidyl ether of bisphenol A typically contain less than 800 parts per million (ppm) of phenolic hydroxyl groups which represents more than 98 percent conversion of the phenolic hydroxyl groups employed in preparing the epoxy resin. A higher molecular weight epoxy resin having an EEW from greater than 2000 to 4000 typically contains less than 2500 ppm of phenolic -OH groups which represents more than 95 percent conversion of the
35 phenolic hydroxyl groups.

Any residual phenolic hydroxyl groups in the advanced resin have been stated to cause viscosity instability of the resulting resin mixture, particularly at elevated temperatures. As a means for controlling the viscosity breakdown of the resin due to the unreacted phenolic

hydroxyl groups, U.S. Patent 3,842,037 suggests adding a strong, inorganic acid when at least 85, more preferably at least 95, percent of the phenolic hydroxyl groups employed in the advancement reaction have been reacted.

Alternatively, in another method for preparing a high molecular weight epoxy resin, U.S. Patent 3,352,825 teaches condensing a dihydric phenol with an excess of epichlorohydrin in the presence of a catalyst such as an alkali metal or ammonium salt of an inorganic monobasic acid to form an intermediate having a free hydroxyl content in the range of from 0.2 to 0.5 phenolic hydroxyl groups per mole of said dihydric phenol. Subsequently, the excess epichlorohydrin is removed and the intermediate condensate subsequently dehydrohalogenated, using caustic alkali and simultaneously the free phenolic hydroxyl groups are reacted with the epoxy groups formed in situ.

Unfortunately, increasing the molecular weight of an epoxy resin also generally increases the melt and solution viscosities of the resin. Such increase in melt and solution viscosities renders the application of the epoxy resin in powder form as a surface coating more difficult. Viscosity represents the resistance to flow of coalesced powder particles. Surface tension provides the driving force for coating flow. Reduced flow may cause an "orange peel" appearance of the coating. P. G. de Lange, Film Formation and Rheology of Powder Coatings, 56 *J. Coatings Technology* No. 717, October 1994 pp. 23-33.

One method by which the melt and solution viscosities of an epoxy resin can be reduced for a given EEW is by regulating the chain growth of the advanced resin by the preparation of a reaction product of a polyepoxide and a polyol wherein the reaction product contains both epoxy groups and terminal hydroxyl groups. The prior art U.S. Patent 4,722,981 teaches an epoxy resin having both epoxy and terminal hydroxyl end groups in an amount of at least 0.25 weight percent each of the epoxy groups and the terminal hydroxyl groups, said weight percent being based on the total weight of the epoxy resin reaction product. Such resin is useful as a starting material for the present invention.

However, despite the improvement represented by the resin of U.S. Patent 4,722,981 to the art, such resin has characteristics in a coating formulation which limit its utility to a substrate capable of withstanding the relatively severe curing conditions of the powder coating.

In order to be economically viable the presently practiced and prior art powder coatings require curing at 160 to 200°C. Lower cure temperatures could make powder coating useful for temperature-sensitive substrates such as wood and thermoplastics.

Solvent-borne coating systems may be formulated which require no elevated temperature for curing. Consequently, heat-sensitive substrates may be coated with solvent epoxy coating systems. The volatile organic solvents required by solvent-based systems are asserted to be unfriendly to the environment. Powder coatings essentially free of volatile components and curable on temperature-sensitive substrates offer an opportunity to reduce

solvent emission to the environment and still provide an effective coating on heat sensitive substrates.

Existing epoxy resin coating systems may be cured at temperatures below 160°C over a substantial time, that is, a bisphenol A epoxy resin coating may be cured with a bisphenol A type phenolic hardener at 120°C for 20 to 22 minutes. It is generally observed that lower viscosity of the coating at the melt temperature yields better adhesion for otherwise comparable resins (see, P. G. de Lange). Lower molecular weight resins and hardeners generally exhibit lower viscosity than comparable higher molecular weight resins and hardeners.

However, a solution to inadequate wet-out, and therefore poor adhesion of the coating to the substrate is not resolvable simply by reducing resin molecular weight. Reduced molecular weight generates a separate countervailing consideration. Reduced molecular weight also generally correlates with reduced softening point and lower glass transition temperature, T_g , of the resin. The reduced softening point may result in clumping and adhesion of the resin particles on storage, reducing the shelf-life of the resulting powder coating and producing a coating with unsatisfactory smoothness.

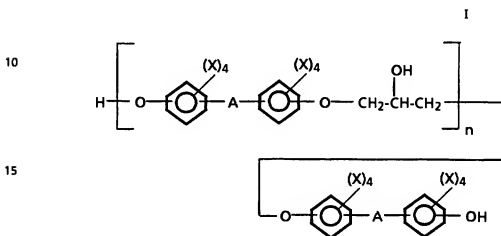
What is needed is an epoxy powder coating having low viscosity at a lower curing temperature thereby providing good coating wet-out on a temperature sensitive substrate while maintaining a sufficiently high softening point/ T_g of the resin component(s) to give adequate shelf life. Of course other requirements of good coatings are also necessary such as; good flow (no "orange peel" appearance), good flexibility, high gloss and corrosion resistance. Use of such a coating is not precluded on a non-temperature-sensitive substrate wherein further improvements of properties such as flow and appearance may be realized.

The present invention provides an epoxy resin useful for a powder coating having a low viscosity at a low cure temperature, having good flow and coating wet-out, and gloss, with high flexibility and protective coating properties, yet providing a softening point/ T_g sufficient to provide adequate shelf-life. More specifically, the present invention is an epoxy resin comprising the reaction product of a polyepoxy and a polyol wherein the reaction product contains both epoxy groups and terminal phenolic hydroxyl groups in an amount of at least about 0.2 weight percent of each of the epoxy groups and the terminal phenolic hydroxyl groups, said weight percent being based on the total weight of the epoxy resin reaction product, wherein the improvement comprises addition, subsequent to the first reaction stage, of epoxidized phenol-formaldehyde resin having a M_n of at least 450, a ratio of M_w/M_n greater than 1.05 and having an epoxy functionality greater than 2.

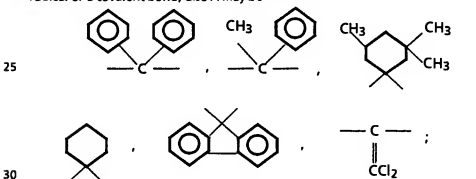
In one embodiment, the instant invention is an epoxy resin comprising the reaction product of a polyepoxy and a polyol wherein the reaction product contains both epoxy groups and terminal phenolic hydroxyl groups in an amount of at least about 0.2 weight percent of each of the epoxy groups and the terminal phenolic hydroxyl groups, said weight

percent being based on the total weight of the epoxy resin reaction product, wherein the improvement comprises addition of an epoxidized phenol-aldehyde resin having an epoxy functionality greater than 2.

- In another embodiment, the instant invention is a method of making an epoxy resin composition comprising combining under isothermal reaction conditions a polyol reactant according to Formula I

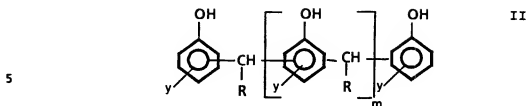


- wherein each A is independently -S-, -S-S-, -C(O)-, -S(O)-, -S(O)₂-, a divalent hydrocarbon radical containing from 1 to 8 carbon atoms or an oxygen, sulfur, or nitrogen containing hydrocarbon radical or a covalent bond; also A may be

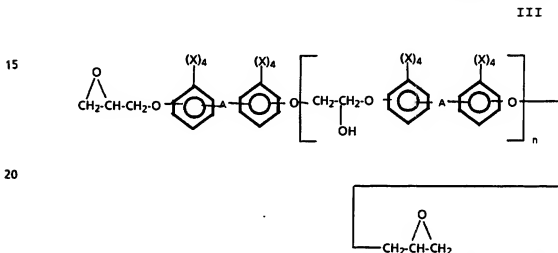


each X is independently hydrogen, halogen, or an alkyl group containing from 1 to 4 carbon atoms, and n has an average value of 0 to 5, preferably from 0 to 2;

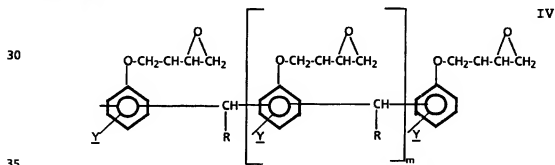
or Formula II



wherein each R is individually hydrogen or an alkyl radical having from 1 to 4 carbon atoms,
 each Y is independently hydrogen, chlorine, bromine or a lower alkyl group having from one to
 10 four carbon atoms and m has an average value from greater than 0 to 10,
 or mixtures of compositions of Formula I and II and an epoxy reactant according to Formula III



25 wherein each A and X are as described previously in the description of Formula I and n has an
 average value of 0 to 4;
 or Formula IV



wherein R, Y and m are described as above with reference to Formula II; or polyglycidyl ethers
 of polyglycols such as the diglycidyl ether of polypropylene glycol, or the polyglycidyl ethers of
 tris(phenol)methane, or a triglycidyl ether of a triazine, for example triglycidyl isocyanurate, or

a mixture of such epoxy reactants such that the epoxy component and the hydroxy component are present in a ratio from 0.1:1 to 10:1, a reaction catalyst inhibiting the reaction progress at a predetermined conversion of reactants at which point the resin has at least about 0.2 weight percent terminal hydroxyl end groups and at least about 0.2 weight percent epoxy end groups.

5 A resulting coating composition exhibits reduced viscosity upon melting when compared to a similar composition without the epoxidized phenol-formaldehyde resin. Hence, from this resin composition a powder coating with improved flow, therefore greater wet-out and improved adhesion results.

The epoxy resins of the present invention offer a significant number of
10 advantages over conventional epoxy resins, which are converted to the extent that no further significant advancement reaction between epoxy and hydroxyl end-groups occurs in a reasonable time (sometimes called "fully converted") and contain essentially no terminal hydroxyl groups. The melt and solution viscosity of the new resins are reduced when compared to fully converted resins of the prior art having similar composition. For resins having a given
15 melt viscosity at a given temperature, the new resins provide a higher T_g which correlates reasonably well with softening point and therefore longer shelf-life than fully converted resins of the prior art having similar melt viscosities at the same temperature.

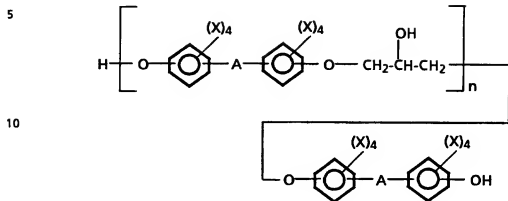
Due to the fact that such resins contain both epoxy and terminal hydroxyl groups, they can constitute a convenient, homogeneous, one-component system which need not
20 require an additional hardener. Such resins can be formulated into a powder coating by the addition of an accelerator only.

The epoxy resin coating composition of the instant invention is comprised of polyhydric alcohol containing an average of more than one hydroxyl group, preferably 1.8 or more hydroxyl groups per molecule, reactive with the epoxy groups of a polyepoxide. The
25 polyols can be saturated or unsaturated aliphatic, cycloaliphatic, aromatic or heterocyclic compounds which can be substituted with one or more non-interfering substituents such as halogen atoms or ether radicals. In general, the preferred polyols are polyhydric phenols. The polyhydric phenols advantageously employed in preparing the epoxy resins are polyhydric phenols represented by the following structural Formula I:

30

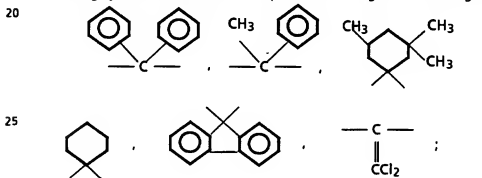
35

I



15

wherein each A is independently a covalent bond, -S-, -S-S-, -C(O)-, -S(O)-, -S(O)₂-, a divalent hydrocarbon radical containing from 1 to 8 carbon atoms or an oxygen, sulfur, or nitrogen-containing hydrocarbon radical, or a composition according to the following description:

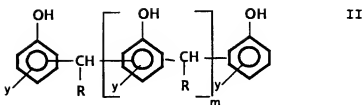


wherein each X is independently hydrogen, halogen or an alkyl group containing from 1 to 4 carbon atoms; and n has an average value of 0 to 5, preferably from 0 to 2; and the phenol-aldehyde condensate resins of the Formula (II):

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wherein each R is individually hydrogen or an alkyl radical having from 1 to 4 carbon atoms, each Y is independently hydrogen, chlorine, bromine or a lower alkyl group having from one to
 10 four carbon atoms and m has an average value from 0 to 10. Mixtures of one or more polyhydric phenols are also suitably employed herein.

Preferably, the polyhydric phenol is a polyhydric phenolic compound of the general structural Formula I wherein A is a divalent hydrocarbon radical having from 1 to 8 carbon atoms, each X is hydrogen, and n has an average value of from 0 to 0.5, more preferably
 15 0. Most preferred of the polyhydric phenols is 2,2-bis(4-hydroxyphenyl)propane, commonly referred to as bisphenol A (BPA).

The initially reacted polyepoxide component useful in preparing the epoxy resin of the present invention is a compound having two or more epoxide groups. The polyepoxides can be saturated or unsaturated aliphatic, cycloaliphatic, aromatic or heterocyclic compounds
 20 and can be substituted with one or more non-interfering substituents such as halogen atoms or ether radicals which are not reactive with the epoxy or hydroxyl groups under the conditions at which the resins are prepared. The polyepoxide component which is reacted with the polyol to form the resin can be monomeric or polymeric.

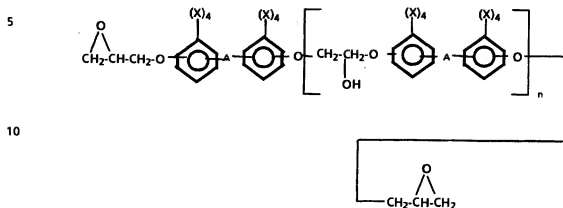
Illustrative examples of epoxy resins useful are described in The Handbook of
 25 Epoxy Resins by H. Lee and K. Neville, McGraw-Hill, New York, 1967, pp. 4-35 through 4-56.

Polyepoxides of particular interest in the practice of this embodiment include the polyglycidyl ethers of bisphenol compounds represented by the general structural Formula III:

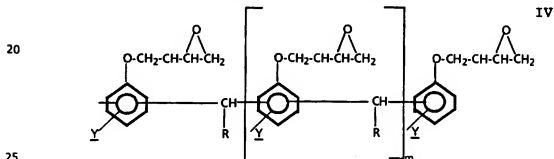
30

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III



- 15 wherein each A and X are as described above in the description of Formula (I) and n has an average value of 0 to 4, preferably 0 to 2, most preferably from 0 to 0.5; the polyglycidyl ethers of a novolac resin, that is, phenol-aldehyde condensates of Formula IV:



- wherein R, Y and m are described as above with reference to Formula (II); polyglycidyl ethers of polyglycols such as the diglycidyl ether of polypropylene glycol; and the polyglycidyl ethers of tris(phenol)methane, or triglycidyl isocyanurate. Mixtures of one or more polyepoxides are also suitably employed herein. Preferred polyepoxides are the liquid polyglycidyl polyethers of a bisphenol, particularly the diglycidyl ether of bisphenol A; the polyglycidyl polyethers of a tetrabromobisphenol, particularly the diglycidylether of tetrabromobisphenol A and mixtures thereof.
- 30

- The polyepoxide and polyol are advantageously employed in an amount such that the number of epoxy equivalents in the polyepoxide to the number of hydroxyl equivalents of the polyol is from 0.1:1 to 10:1. Preferably, the polyepoxide and polyol components are employed in a ratio from 0.3:1 to 5:1, more preferably from 0.3:1 to 2:1, epoxy equivalents to hydroxyl equivalents. The relative proportions of the polyepoxide and polyol
- 35

components most advantageously employed will be dependent on a variety of factors including the specific polyepoxide and polyol employed and the desired properties of the epoxy resin prepared therefrom.

- 5 In preparing the resins, the polyol and the polyepoxide components are contacted in the presence of a catalyst for the reaction between the hydroxyl groups of the polyol and the epoxy groups of the polyepoxide and at conditions sufficient to form the desired resin. Preferably, this reaction is conducted neat, that is, in the absence of any reaction diluent or solvent.

- Materials capable of catalyzing the stated reaction are well-known in the art and reference is made thereto for the purposes of this invention. Illustrative catalysts are set forth
10 in U.S. Patents 2,633,458; 2,658,855; 3,377,406; 3,694,407; 3,948,855; 4,389,520; 4,354,015; and 3,477,990 and *The Handbook of Epoxy Resins* by H. Lee and K. Neville, pp. 11-13 to 11-23. Representative of the described catalysts are secondary and tertiary amines, preferably tertiary amines such as benzyl dimethyl amine, triethyl amine and benzyl diethyl amine; the alkali
15 metal hydroxides for example, potassium hydroxide; quaternary ammonium compounds such as tetraalkylammonium halides, for example, tetramethyl ammonium chloride and phosphines and quaternary phosphonium salts such as triphenyl phosphine and ethyl triphenyl phosphonium acetate.

- The catalyst is typically employed in conventional amounts. These amounts will
20 vary depending on the specific catalyst, polyepoxide and polyol employed but will preferably vary from 0.001 to 1 weight percent based on the total weight of the polyol and polyglycidyl ether components. More preferably, from 0.01 to 0.25 weight percent of the catalyst is employed, said weight percent being based on the total weight of the polyol and polyepoxide components.

- 25 Although not preferred, the reaction of the polyol and polyepoxide components can be conducted in the presence of a reaction diluent. If employed, the reaction diluent is preferably a solvent for, or miscible with, both the polyol and polyepoxide component. Representative solvents which can be employed include various glycol ethers such as ethylene glycol monomethyl ether, or propylene glycol monomethyl ether and esters thereof such as
30 ethylene glycol monoethyl ether acetate; ketones such as methyl isobutyl ketone, methyl ethyl ketone and acetone; and aromatic hydrocarbons such as toluene, xylene or mixtures thereof. If employed, the organic liquid reaction diluent is generally employed in an amount from 5 to 300 percent based on the total weight of the polyol and polyepoxide components.

- The reaction of the polyol and polyepoxide is advantageously carried out at an
35 elevated temperature, preferably from 60°C to 200°C, more preferably from 100°C to 180°C. The reaction is continued until the desired conversion, as determined by monitoring a measurable parameter such as the residual epoxy and terminal hydroxyl content in the resin, or melt viscosity. The reaction is effectively terminated at the desired end point.

A convenient method of predicting the approximate time at which a desired characteristic of the resin will be arrived at includes conducting the reaction under essentially isothermal conditions at laboratory scale by terminating the reaction at various times and measuring the extent of reaction by means of measurement of physical or chemical parameters such as melt viscosity and residual hydroxyl content in the ordinary manner known by those skilled in the art.

Any method which effectively inhibits further reaction upon reaching the desired degree of conversion can be employed herein. The reaction is effectively inhibited when the rate of reaction of the hydroxyl and epoxy group is sufficiently reduced such that further reaction, if any, does not significantly and deleteriously affect the product or its handling characteristics. Preferably, the reaction is sufficiently inhibited such that the viscosity of the resin remains essentially constant or increases only marginally with time. For example, upon reaching the desired degree of conversion the reaction mixture can be quenched to stop the reaction. However, the rapid quenching of the reaction mixture must be conducted carefully to prevent clotting or lumping of the resin and to prevent the resin from forming a large solid mass which cannot subsequently be used.

A convenient method for cooling the reaction mixture comprises the addition of a solvent to the mixture, thereby diluting the mixture and reducing its temperature. The amount of organic solvent to be added is dependent on the reaction temperature and the temperature at which reaction is effectively terminated. The addition of organic solvent to the reaction mixture is particularly preferred when the resin is subsequently to be applied from solution.

A preferred method for inhibiting the reaction comprises adding a material to the reaction mixture which effectively inhibits further reactions such as by deactivating the catalyst, or by interrupting the reaction mechanism, thereby inhibiting further reactions between the polyol and the polyepoxide.

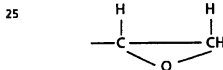
Strong inorganic and organic acids and the anhydrides and esters of said acids (including half esters and part esters) have been found to be particularly effective as reaction inhibitors. By the term "strong acid" it is meant an organic acid having a pK_a value below 4, preferably below 2.5. Representative reaction inhibitors include inorganic acids such as hydrochloric acid, sulfuric acid and phosphoric acid; inorganic acid anhydrides such as phosphoric acid anhydride (P_2O_5); esters of inorganic acids such as dimethyl sulfate; the organic acids such as alkyl, aryl and aralkyl and substituted alkyl, aryl and aralkyl sulfonic acids such as p-toluene sulfonic acid and phenyl sulfonic acid and stronger organic carboxylic acids such as trichloroacetic acid and alkyl esters of said acids, such as the alkyl esters of p-toluene sulfonic acid, for example, methyl-p-toluene sulfonate, and ethyl-p-toluene sulfonate and methane sulfonic acid methyl ester. An example of an acid anhydride of a strong organic acid that can be employed herein is p-toluene sulfonic acid anhydride. Of the reaction inhibitors, the alkyl esters of sulfuric acid; the aryl or aralkyl sulfonic acids and the alkyl esters of said acids

are preferably employed herein. Most preferably, an alkyl ester of para-toluene sulfonic acid, particularly methyl or ethyl-p-toluene sulfonic acid is employed as the reaction inhibitor herein.

The amounts of reaction inhibitor added to the reaction mixture are dependent on the specific inhibitor employed and the catalyst employed in preparing the resin. In general, the inhibitor is added in an amount sufficient to overcome the catalytic activity of the catalyst. Preferably, at least 0.9, more preferably at least 2, equivalents of the inhibitor are added for each equivalent of the catalyst employed. Although the maximum amount of inhibitor added to the reaction mixture is dependent on the desired properties of the resin and the expense of adding excess inhibitor, the inhibitor is preferably added in an amount not exceeding 5 equivalents for each equivalent of catalyst in the reaction mixture.

The resin of the instant invention may also be prepared by reducing the temperature of the reaction components. Additional temperature control may be achieved over the reaction components by conducting the reaction in an extruder having zones of temperature control. A zone of high temperature may be useful to heat the reaction components sufficient to destroy the catalytic activity of any catalyst present. Additionally, an inhibitor may be added to the reaction components to interrupt the activity of a catalyst or by another mechanism to halt the reaction of reaction components. Termination of a reaction by temperature reduction has the advantage that the resin does not contain an inhibitor required by quenching the batch-wise reaction by inhibitor addition.

The reaction is terminated at a point such that the resulting resin contains the desired amounts of epoxy groups and terminal hydroxyl groups. In this invention, the resin will contain at least 0.2 percent, by weight, of each of the epoxy and terminal hydroxyl groups. The term "epoxy group" means a radical of the following structural formula:



30 having an equivalent weight percent of 43. The term "terminal hydroxyl group" means a terminal hydroxyl group having an equivalent weight of 17.

The weight percent of epoxy groups in epoxy resin may be determined according to the method disclosed in U.S. Patent 4,722,981.

These weight percentages can also be viewed as the numbers of equivalents of the epoxy and hydroxyl groups per kilogram of the resin reaction product. It has been determined that 0.2 weight percent of the epoxy group is about 0.0465 epoxy equivalents per

kilogram resin produced. Similarly, 0.2 weight percent of the hydroxyl group is about 0.12 hydroxyl equivalents per kilogram resin produced.

The hydrolyzable chloride content of the resin is generally less than 1 and often less than 0.5 percent based on the total weight of the epoxy resin reaction product. However, a hydrolyzable chloride content of up to 5, preferably not more than 2, weight percent based on the total weight of the epoxy resin reaction product may be tolerated. The amounts of hydrolyzable chloride are determined for the purpose of this invention by the method described in The Handbook of Epoxy Resins pp. 4-29 and 4-30 (Table 4-23).

Although the amount of epoxy groups and terminal hydroxyl groups most advantageously contained by the resin is dependent on the desired properties of the resin, for example, its solution viscosity, the resin preferably contains at least 0.5, more preferably at least 1, weight percent of epoxy groups and at least 0.2 weight percent of terminal hydroxyl groups. The said weight percents are based on the total weight of the resin. In general, the resin preferably comprises less than 20, more preferably less than 12, weight percent of epoxy groups and less than 10, more preferably less than 7 weight percent of the terminal hydroxyl groups.

In the first stage of preparation of the resin, conversion of the polyol and polyepoxide components is controlled such that the resin contains the desired amounts of epoxy and hydroxyl groups. This conversion is dependent on the amount of polyol and epoxide employed. Advantageously, at least 45 percent and up to 95 percent of the deficient component present is reacted. If the components are employed in equivalent amounts, then at least 45 percent and up to 95 percent of both components are reacted. Preferably, at least 50, more preferably at least 55, and up to 95, more preferably up to 90, most preferably up to 85, percent of the deficient component or the equivalent reactants, as the case may be, are reacted.

The number average molecular weight of the resin is dependent on the desired end-use application of the resin and the physical and chemical properties required for said end-use. Preferably, the resins have a molecular weight of less than 10,000. More preferably, the resins will possess molecular weights of less than 4000, most preferably less than 2000, and more preferably more than 300, most preferably more than 500.

In the practice of the present invention, the polyepoxide can be advanced with a polyol and, optionally, a polyacid to completion (thereby forming a resin having either only epoxy groups or terminal hydroxyl groups depending on which reactant is employed in excess) in one reaction step and thereafter reacted with a polyol or a polyepoxide component to form the resin. The advancement of epoxides with diacids is discussed in Madec, P-J et al., Advances in Polymer Science, 71 (1985) 153 - 224; U.S. Patent 4,722,981 Example 18.

At a second reaction stage starting from the first stage reaction product leaving unreacted hydroxyl and epoxy groups, there is added to the resin a compound having an

average functionality greater than 2. This component lowers the viscosity at the cure temperature and reacts with the first stage reaction product. Thus the second stage addition component may be described as a "reactive diluent."

- 5 As the resin prepared by the first reaction stage has available both hydroxyl and epoxy end groups, the added compound suitable for crosslinking at the second stage may be either hydroxyl reactive or epoxy reactive.

As hydroxyl reactive compounds suitable for addition at this second stage the polyglycidyl ether of an aldehyde-phenol condensate resin described previously with reference to Formula IV are suitable.

- 10 For such polyglycidyl ethers the range of m should be on average from greater than zero to 5.0, more preferred in a range of from 0.5 to 4.5. Also suitable, is a mixture of polyglycidyl ethers containing in the mixture polyglycidyl ethers according to Formulae III and IV with a range of m and n as noted. In such mixtures it is beneficial that there be at least 5 percent, preferably 12 percent more preferably 25 percent of the reactive hydroxy component
15 of a second stage addition, of a compound having an average functionality greater than 2. The remaining hydroxy reactive components of the secondary addition may have an average functionality of 2 or less, but more than 1.2. Diluents or solvents may be present in the second stage. The diluent content is advantageously less than 50 percent of the total composition, by weight.

- 20 As epoxy reactive compounds suitable for additives at this second stage, the polyhydric phenols described with reference to Formula II is suitable. For such polyhydric phenols, the range of m should be an average from greater than zero to 5.0, preferably from 0.5 to 4.5. Also suitable is a mixture of polyhydric phenols containing in the mixture polyhydric phenols according to Formulae I or II with a range of m and n as noted. In such mixtures it is
25 beneficial that there be at least 10 percent, preferably 20 percent, more preferably 25 percent of the epoxy reactive component of a second stage addition of a compound having an average functionality greater than 2. Diluents or solvents may be present in the second stage. The diluent content is advantageously less than 50 percent of the second stage composition by weight.

- 30 Certain preferred embodiments of the instant invention demonstrate significant advantages as epoxy resins curable at comparatively low temperatures with performance properties improved over the prior art, specifically as coating materials.

- Upon termination of the reaction at a further stage, the resin can be formulated into a number of different compositions for use in a variety of end-use applications. For
35 example, the resin can be admixed with an accelerator and, optionally, other adjuncts such as flow control agent to form a powder coating composition. Although a hardener may be added to the resin component, since the resin contains both unreacted epoxy and unreacted terminal hydroxyl groups, the resin may be cured without addition of hardener.

Hardeners, catalysts and accelerators conventionally employed in epoxy resin-based powder coating compositions can be employed in a powder coating composition of the resin. Such hardeners and accelerators are well-known in the art and reference is made thereto for the purposes of this invention. Representative accelerators include stannous salts of monocarboxylic acids, such as stannous octoate and stannous laureate, various alkali metal salts such as lithium benzoate, certain heterocyclic compounds such as imidazole and benzimidazole compounds and salts thereof, onium compounds such as quaternary ammonium and phosphonium compounds and tertiary amines phosphines, and phenol carbamates.

Preferred accelerators for use in preparing the powder coating formulations are those which are solid at room temperature and include the imidazoles, particularly the alkyl substituted imidazoles such as 2-methyl imidazole, solid phosphines or amines such as triphenyl phosphine, quaternary phosphonium, and quaternary ammonium compounds.

In preparing the powder coating composition, the amount of accelerator most advantageously employed will vary depending on the particular accelerator employed. Preferably, the accelerator will be employed in an amount from 0.01 to 5 weight percent based on the weight of the resin. More preferably, the accelerator is employed in an amount from 0.02 to 3 weight percent based on the weight of the resin.

Representative of the optionally employed hardeners are phenolic hardeners such as phenolic or cresol novolacs and the phenolic hardeners as described in British Patent Specification No. 1,429,076, dicyandiamide, acid anhydrides such as trimellitic anhydride, the acid functional polyesters, and hydrazides such as adipic dihydrazide and isophthalic dihydrazide. If employed, the hardeners are generally employed in an amount from 1 to 50 weight percent based on a total weight of the resin.

It has been found that the number of equivalents of epoxy groups per kilogram of resin in the second stage reacted resins suitable for use as powder coatings is 1.54 to 2.1. A maximum number of epoxy equivalents is 5.9. Excess epoxy equivalents results in low softening points. More preferably the range of epoxy equivalents is more than 4.1 per kilogram resin. Most preferably, the resins contain from 5.4 to 5.9 epoxy eq/kg of epoxy resin prior to conversion of any of the epoxy groups to epoxy-derived groups. The resin contains 0.2 to 1.5 eq/kg of terminal phenolic hydroxyl groups. It is found not only that the above ranges of hydroxyl group and epoxy group concentrations are necessary in the controlled conversion resins to produce epoxy resins especially good for solution coating formulations, but surprisingly upon further conversion of at least a portion of the epoxy groups of these controlled conversion resins to epoxy-derived groups such as alpha-glycol or phosphate ester groups, curing times are substantially reduced as compared with resin having no further conversion of epoxy end-groups, while good resin and coating properties are maintained.

In general, the epoxy groups of the controlled conversion resin can be converted to any epoxy-derived functional groups that will not detrimentally affect the curing reaction.

Although the present invention is in no way limited by such theory, it is believed that a hydrolysis reaction of the epoxy group with added water forms alpha-glycols. Thus, water addition is a way to conveniently convert the epoxy groups to suitable epoxy-derived groups. In this regard, the number of equivalents of epoxy groups will determine the amount of water or other reactant necessary to form the alpha-glycol and possibly other types of epoxy-derived groups. In general, water is used in excess amounts of from 0.5 to 20 weight percent based on the total resin weight, preferably 1 to 10 weight percent.

Reaction of the resins with water and acid can also be employed to convert the epoxy groups. It is theorized that this is a conversion of the epoxy groups to alpha-glycols and acid esters and possibly other types of groups derived from the epoxy groups, but the present invention is not to be limited by this theory. Water and acid are used generally in amounts of 0.2 to 10 weight percent acid. These weight percentages are based on the total weight of the resin to which the water and acid are added. More preferably, the respective weight percentages of water and acid are 0.5 to 3 weight percent and 0.2 to 2 weight percent.

In one method of practicing the present invention, the epoxy groups of the controlled conversion resin are reacted with water and a phosphorous-containing acid. In this embodiment, the amounts of water and phosphorous-containing acid (preferably phosphoric acid) are balanced to maximize the mono-esters and minimize the tri-esters. It has been found generally that when the phosphorous-containing acid is used in this way with a controlled conversion resin it should be added in amounts of from 0.1 to 3 weight percent based on the resin weight, preferably from 0.2 to 1.5 weight percent while the water used in conjunction should be added in amounts of from 0.2 to 10 weight percent based on the resin weight, preferably from 0.5 to 3 weight percent.

In another embodiment of the present invention, in step one, amounts of water and acid, preferably a phosphorous-containing acid, are employed as a reaction inhibitor in preparing the controlled conversion resins. The amount of water and acid added is in excess of amounts taught to inhibit the polyol polyepoxide reaction, which excess amount is then able to react with the epoxy groups of the controlled conversion resin to form the epoxy-derived groups. Preferably, the above-described mixture of such groups comprise alpha-glycols and phosphorous-containing acid esters. When used in this fashion to both inhibit the reaction, and convert the epoxy groups to epoxy-derived groups, the acid is used in amounts of from 0.1 to 3 weight percent based on the weight of resin, preferably from 0.2 to 1.5 weight percent.

It may be observed that by converting at least about 30 percent of the epoxy groups of a resin to epoxy-derived groups, that the curing rate may be increased and the overall cure time required shortened thereby. Preferably more than about 50 percent and most preferably substantially all the epoxy groups are converted to epoxy-derived groups. Although containing substantially no epoxy groups, such resins are referred to herein as epoxy resins in view of their origin. Of course when the reaction is inhibited and the epoxy groups are

converted in a single step and/or by a single reactant such as phosphoric acid, there is not necessarily isolated a controlled conversion resin having a specific epoxy group content. In these types of situation, within the scope of the present invention, the reduced number of epoxy groups remaining in the final resin product (if any) and the presence of the epoxy-

5 -derived groups will be indicative of the practice of the present invention, and will produce the improved resins thereof.

Alternatively, following preparation of the resin, the resin may be dissolved in an organic liquid for subsequent use. Suitable organic liquids for preparing the organic liquid solution of the resin are dependent on the particular resin and the amounts of terminal

10 hydroxyl and epoxy groups in the resin. In general, alcohols such as n-butanol, glycol ethers such as propylene glycol monomethyl ether and esters thereof, ketones, aliphatic or aromatic hydrocarbons such as xylene and chlorinated aliphatic and aromatic hydrocarbons are preferred.

In preparing an organic liquid solution of the resin, it is generally desirable to

15 employ a hardener which is also soluble in the organic liquid. Such hardeners are well-known in the art and reference is made thereto for the purposes of this invention. Representative hardeners include phenolic resins such as the reaction product of phenol with an excess of formaldehyde and other hydroxymethyl-containing benzene derivatives and alkylated derivatives thereof and amine-aldehyde condensates, commonly referred to as "aminoplast" or

20 "aminoplastics" which are the condensation products of an aldehyde with an amine such as melamine, urea and benzoguanamine and the alkylated derivatives thereof.

The amount of the hardener most advantageously employed is dependent on a variety of factors including the end-use application for the organic liquid solution and the desired physical and chemical properties of said end-use application. Preferably, from 1 to 50

25 weight percent of the hardener are employed based on the total weight of the resin and hardener.

In addition, it is often desirable to add a small amount of an inorganic acid to the organic liquid solution as a catalyst for the reaction of the resin with the hardener. In general, the inorganic acid is preferably phosphoric acid and is used in an amount from 0.1 to 5 weight

30 percent based on the total weight of the organic liquid solution.

The solids concentration at which the organic liquid solution is prepared is dependent on various factors including the desired viscosity of the resulting solution. In general, the organic liquid solution is formulated such that the solids content is as high as possible while maintaining a sufficiently low viscosity for effective application. Since the resins

35 exhibit a lower solution viscosity than conventional resins which would possess equivalent cured properties, the organic liquid solution of a resin can generally be prepared at higher solids concentrations than an organic liquid solution of a conventional resin. For example, a resin useful in coating applications may be formulated as an organic liquid solution which

comprises at least 40 percent of the resin and any hardener employed based on the total weight of the organic liquid solution. More preferably, the liquid solution contains at least 50 percent, most preferably from 50 to 70 weight percent of the resin and hardener.

- 5 Powder coatings prepared from resins according to the instant invention demonstrate advantageous properties over prior art making such resin particularly useful for coating applications. Coatings advantageously form a uniform surface on the substrate (see, P.G. de Lange).

- 10 Powder coatings prepared from resin according to the instant invention advantageously demonstrate low viscosity under curing conditions. A particular further advantage of low viscosity may be obtained by the inclusion of an epoxidized phenol-formaldehyde resin to the first stage reactant.

- 15 The cure of an epoxy resin depends on the temperature of the cure and the duration. The inventive resin cures under conditions of lower temperature than the prior art. The resin curing is achieved over a shorter time than a prior art of a similar composition. Moreover cured coating compositions prepared from resin of the instant invention demonstrate coating properties consistent with the prior art, in spite of the milder curing conditions. Prior art resins exist which are curable at similar curing temperatures to the resins of the instant invention. However, the instant resin exhibits a higher T_g /softening point and therefore a longer shelf-life.

- 20 These and other advantages will be apparent from the following examples:

Example 1

- In a nitrogen atmosphere 2760 parts by weight diglycidyl ether of bisphenol A was combined with 1310 parts of bisphenol A in the presence of 1.4 parts of ethyl triphenyl phosphonium acetate. The combination was warmed to 120°C and gradually the temperature was increased to 150°C and maintained at 150°C over a period of 1 to 5 hours until a desired melt viscosity measured at 120°C of 1 to 6 Pa·s is attained. At the desired viscosity, 1 part of methyl-4-toluenesulphonate was added to the combination and mixed for 20 to 30 minutes. Optionally, a flow agent pigment, levelers or other ingredients could be added at this point if desired. 930 parts of an epoxidized phenol-formaldehyde resin having an M_n of 534 and $M_w/M_n = 1.7$ (5.2 equivalents) pre-heated to 90°C was added to the mixture and further mixed for 10 to 20 minutes.

- The reactor contents were cooled. At room temperature the resin is a solid. The properties of the resin are found as: an epoxy equivalent weight of 450, a softening point of 77.6°C, melt viscosity of 2.5 Pa·s at 120°C, 0.4 Pa·s at 150°C; a number average molecular weight (M_n) of 900, a mass average molecular weight (M_w) of 2340, and a ratio of molecular weight ($M_w/M_n = 2.6$)

Examples 2-9

For Examples 2 through 8, the steps according to Example 1 were repeated incorporating the ingredients as indicated on Table I. Example 9 was prepared using an extruder as described for examples 20 through 24. Resins having the properties noted are prepared.

5 Example 10 (not an example of the invention)

67.9 Parts of diglycidyl ether of bisphenol A and 32.1 parts of bisphenol A were combined in the presence of 0.05 parts of ethyl triphenyl phosphonium acetate. The composition was heated with mixing to 150°C and the reaction permitted to continue adiabatically for three hours until the bisphenol A was believed completely reacted. The
10 adiabatic reaction heated the mixture to 190°C. Then an epoxidized phenol-formaldehyde resin having an epoxy functionality of 3.6, M_n of 534 and $M_w/M_n = 1.7$ was added to the liquid mixture, in an amount to prepare a composition having an epoxidized phenol-formaldehyde resin content according to Table II. The composition is permitted to cool to room temperature. The resin composition properties are noted in Table II.

15 Example 11

Over a blanket of nitrogen gas there was added to a vessel for reaction 22.36 parts of diglycidyl ether of bisphenol A, 10.33 parts bisphenol A, ethyltriphenyl phosphonium acetate catalyst (207 ppm). The reactants were heated to 120°C with continuous stirring. Samples were removed periodically and tested for viscosity as a means of determining the
20 extent of completion of reaction. It was projected from the viscosity of the removed samples that after about 6 hours a predetermined target viscosity would be attained. The reaction progress was halted by the addition with continued stirring of methyl p-toluene sulphonate 0.008 parts. Stirring continued for 10 minutes. 7.5 Parts of an epoxidized phenol-formaldehyde resin having M_n 534 and M_w/M_n 1.7 heated to 100°C was added to the vessel.
25 After 3 hours of stirring the composition was removed for testing. Testing the resin disclosed the properties according to Table II.

30

35

Table I

Component in parts by weight		2*	3	4	5*	6*	7	8	9
5	A solid epoxy resin containing 40 wt percent of an epoxidized phenol formaldehyde resin having an epoxy functionality of 3.6, M_n 534, M_w/M_n of 1.7. The composition has an epoxy equivalent weight of 325.		22						
10	Resin according to Example 1 without an epoxidized phenol-formaldehyde resin having an M_n 534, M_w/M_n = 1.7.						44.0		
	Solid epoxy resin EEW = 700-750							39.0	
15	Solid Bis A epoxy resin 4-type with 18.6 % of an epoxidized phenol-formaldehyde resin having an epoxy functionality of 3.6, M_n 534, M_w/M_n = 1.7.			50.3					
20	Solid bisphenol A advanced epoxy resin with epoxy equivalent weight of 495 - 526.		25.4						
	Saturated carboxylated polyester resin . (1)					37.0	26.0	31.0	
	Resin according to Example 1	53.4			53.3	33.0			
25	Diglycidyl ether of bisphenolA, EEW = 180.4, M_n = 422, M_w/M_n = 1.1.								50.3
	Solid, phenolic-type hardener having a hydroxy equivalent weight of 240-270.	15.8	21.7	17.9	16.8				18.7
	MODAFLOW (2)	0.4	0.4	0.5	0.45				0.5
30	Flow Agent (ResiFlow PV5) (3)					1.0	1.0	1.0	

Table I (continued)

	Component in parts by weight	2*	3	4	5*	6*	7	8	9
5	1,3-phenoxy-2-propanol 98% methyl-iso-butylketone 2%					1.0	1.0	1.0	
	TiO ₂ (KRONOS 2310) (4)	25.0	25.0	25.0	25.0	28.0	28.0	28.0	25
	8aSO ₄ (7)	5.0	5.0	5.0	5.0				5.0
	2-methylimidazole	0.45	0.45	0.54	0.5				0.54
10	<u>Observations</u> Gel time at 180° C in seconds (after storage 42 days) Flow (scaled 1 to 4; 1 = level coating 4 = orange peel)	45 (1)	45 1	49 (35) 2	47 (43) (1)	107	293	190	35
15	<u>Impact resistance (8)cm-kq</u> <u>Front/Reverse, steel panel (5)</u> 110°C cure temperature 115°C 120°C	(5) 184/ 184 184/ 184/ 184/ 184	(5) 115/ 34.5 184/5 7.5 184/5 7.5	(5) 34.5/ 34.5 184/ 161 184	(5) 34.5/ 34.5 184/ 184				15 min 184/ 184
20	<u>Indentation, (9)mm, steel panels (5) and (6)</u> 110°C cure temperature 115°C cure temperature 120°C cure temperature 140°C cure temperature - 5 minutes - 20 minutes - 22.5 minutes	(5) 8.8 8.3 8.2	(5) 8.6 8.2 8.6	(5) 0.5 8.7	(5) 0.5 8.5				
25						(6) 7.4 7.5 7.4	(6) 0.5 0.5 0.5	(6) 0.5 1.0 7.4	

* Examples of the Invention

- (1) Uralac P 2980 Available from DSM Kunstharze GmbH, Am Kreisforst 1, D-49716 Meppen, GERMANY.
- (2) MODAFLOW™ polyacrylate flow modifier available from Monsanto Europe SA, Brussels, BELGIUM.
- 30 (3) ResiFlow PV5 polyacrylate flow modifier available from Worlée Chem, Lauenburg/Elbe, GERMANY.
- (4) KRONOS 2310. Titanium dioxide, available from Kronos Titan GmbH, Leverkusen, GERMANY.
- (5) Steel is DIN 1624 - ST4, degreased 1mm thick
- (6) Bonder™ 1041600C, chromate treated, used neat, 1 mm thick. Bonder is a Trademark of Chemetall, Frankfurt/Main, GERMANY.
- 35 (7) EWO, Sachleben Chemie, Duisberg, GERMANY.
- (8) ASTM 614, 20 minutes cure time, unless indicated.
- (9) DIN 53156, 20 minutes cure time, unless indicated.

Table II

	Example 10 (parts by weight)	Example 11* (parts by weight)
5 Diglycidyl ether of bisphenol A	67.9	22.36
Bisphenol A	32.1	10.33
Ethyltriphenyl phosphonium Acetate	0.05	0.0207
10 Methyl p-toluene sulfonate	-	0.008 parts
Epoxide equivalent weight	520	438
wt % epoxide	8.25	9.82
Molecular weight (M_n)	1398	925
Molecular weight (M_w)	4331	2000
15 Mw/Mn	3.1	2.2
An epoxidized phenol-formaldehyde resin having an epoxy functionality of 3.6, M_n 534, M_w/M_n = 1.7	22.9 (18.6%)	7.5 (18.7%)

Examples 12 - 17

- 20 Examples 12-17 compare the properties of epoxy resin compositions having the same ratio of epoxy groups to phenolic groups in the starting materials. All compositions are mixed in a Mixaco container mixer, then melt extruded in a Werner & Pfleiderer ZSK30 extruder at 63°C. After extrusion and cooling, the solid resin is ground to a practical size consistent for all samples from one to one hundred μm having the average particle size distribution at 25 to 40 μm .

Table III presents compositions and coating properties for Examples 11 through 16.

Example 18

- 30 A mixture of 584 parts of the diglycidyl ether of bisphenol A (EEW 178, 3.28 equivalents) was mixed with 316 parts of bisphenol A (2.77 equivalents) and heated with stirring to 95°C under a nitrogen atmosphere. Then, 0.21 parts of a solution of ethyltriphenylphosphonium acetate was added as advancement catalyst/initiator. The temperature was then carefully increased to 125°C where it was held until the melt viscosity of the resin (measured at 120°C with an ICI cone and plate viscosimeter) had a value of 5 Pa.s. Methyl p-
35 toluenesulphonate (0.8 parts) was added, followed by 100 parts of an epoxidized phenol-formaldehyde resin having an epoxy functionality of 3.6, M_n of 534 and M_w/M_n 1.7. An epoxy resin will be obtained with a weight percentage epoxy content in the range of 5 to 12 percent,

- an epoxy equivalent weight of 350 to 900, a Mettler Softening Point of 70 to 100°C, a melt viscosity at 150°C of less than 1.0 Pa·s, at 120°C of between 1 and 5 Pa·s and at 100°C of between 5 and 40 Pa·s, a number average molecular weight in the range of 750 to 1500 (M_n) with a polydispersity in the range of 1.25 to 5.0 and a glass transition temperature (T_g) greater than 30°C which resin is curable as a coating at 90 to 180°C within a 30 to 10 minutes cure time.
- Example 19

- Another resin may be prepared according to Example 17, except that 484 parts of the diglycidyl ether of bisphenol A may be used together with 200 parts of an epoxidized phenol formaldehyde resin having an epoxy functionality of 3.6, M_n of 534 and M_w/M_n of 1.7.
- The other quantities and conditions are the same as in Example 1.

Table III

	12	13	14	15	16*	17
5	FIRST STAGE COMPONENTS					
	Bisphenol A	11.93	17.80	14.33	13.33	11.90
	Diglycidyl ether of bisphenol A	37.80	39.63	38.75	28.39	37.72
	SECOND STAGE COMPONENTS					
				9.5	9.5	
10	Tg °C of Second Stage Resin	29.3	54.0	46.1	46.0	34.0
						-
	FORMULATION WITH HARDENER FOR COATING					
	Solid phenolic type hardener having a hydroxy equivalent weight of 240 - 270	19.82	12.14	16.47	18.30	18.18
						19.77
	2-methyl imidazole	0.45	0.45	0.45	0.45	0.6
15	TiO ₂ (Kronos 2310)	29	29	29	29	29
	MODAFLOW™ III	1	1	1	1	1
	TOTAL parts by weight	100	99.72	100	99.97	99.85
						99.84
	Gel time at 180°C - seconds	63.5	69.0	67.5	47.5	45.0
						52.0
20	PROPERTIES OF COATING ⁽¹⁾					
	Coating thickness μm/ Flow rating ⁽²⁾					
	110°C	73/4.6	77/1.9	75/2.1	83/2.3	63/2.7
	115°C	86/4.6	89/1.7	69/2.0	87/2.3	72/3.8
	120°C	88/4.1	80/1.8	73/2.7	80/1.7	76/4.3
	Impact Test cm·kg					
	P = passed f = failed					
25	front side/back side	f23/f23	f23/f23	f23/f23	f23/f23	f23/f23
	110°C	f23/f23	f23/f23	f23/f23	f23/f23	f23/f23
	115°C	p57.5/	p184/	p184/	p57.5/	p184/
		f23	p184	p184	f23	p184
	Cure Temperature for 25 minutes	120°C	p184/	p184/	p184/	p184/
			p184	p184	p184	p184
	Indentation mm					
30	110°C	0.5	0.5	9.5	2.3	1.0
	115°C	9.5	10.0	10.0	9.5	9.4
	120°C	9.5	10.0	10.0	9.5	9.3

(1) Steel is DIN 1624 - ST4, degreased 1 mm thick.

(2) The Flow Rating measurements are reported according to measurements from a Byk-Gardener wave-scan conducted according to the operating instructions booklet (1992). Byk-Gardner GmbH, D-82538 Geretsried, GERMANY. Ratings are given on a scale of 0 (poor) to 10 (excellent).

(3) An epoxidized phenol-formaldehyde resin having an epoxy functionality of 3.6, M_n 534,

Example 20 - 24

Using a reactive ZSK-30 intermeshing, co-rotating twin-screw extruder operating at 100 resolutions per minute. The barrel is 1410 millimeters in length excluding the die. The barrel is comprised of 11 single length (900 mm) and 2 double length (180 mm) barrel sections with one 30 mm support plate and one 30 mm end plate. The barrel configuration had a feed section, followed by a solid section, a vent section, then alternating plugged ported or solid sections for the remainder of the barrel. The extruder head has pressure measurement, a rupture disc, and piping connection. There were four extensive mixing sections in the screw design, which extended into the extruder head. The barrel was divided into nine heating and cooling zones. The ninth zone is the extruder head. Epoxy resin is prepared from starting materials at the feed rates indicated in Table IV. Zones 1 - 3 operate at 175°C, zone 4 at 220°C, zones 5 and 6 operate at 240°C, Zones 7 - 9 at 175°C.

Table IV

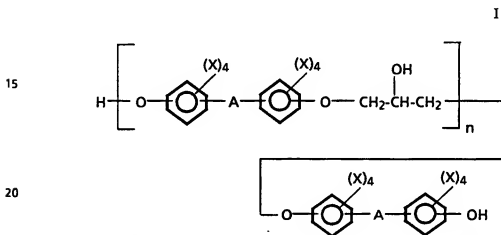
Examples	20	21	22*	23*	24*
Diglycidyl ether of bisphenol A having an EEW of 180.4, Mn = 422; Mw/Mn = 1.1	5.05 kg/h	5.1 kg/h	5.1 kg/h	5.1 kg/h	5.1 kg/h
Epoxydized phenol-formaldehyde resin having an epoxy functionality of 3.6, Mn of 534 and Mw/Mn = 1.7, EEW = 177			1.7 kg/h	1.7 kg/h	1.7 kg/h
Bisphenol A	2.3 kg/h	2.3 kg/h	2.3 kg/h	2.3 kg/h	2.3 kg/h
Ethyltriphenyl phosphonium Acetate	300 ppm	300 ppm	300 ppm	300 ppm	300 ppm
Second Stage Resin Properties: Epoxy equivalent weight Phenol equivalent weight	661 10800	661 9139	440 7217	442 6704	441 7321
Molecular weight: Mn Mw	N.A. N.A.	N.A. N.A.	N.A. N.A.	N.A. N.A.	693 1914

* Examples of the invention

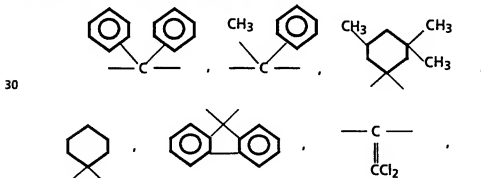
WHAT IS CLAIMED IS:

1. An epoxy resin comprising the reaction product of a polyepoxy and a polyol wherein the reaction product contains both epoxy groups and terminal phenolic hydroxyl groups in an amount of at least about 0.2 weight percent of each of the epoxy groups and the terminal phenolic hydroxyl groups, said weight percent being based on the total weight of the epoxy resin reaction product, wherein the improvement comprises addition of an epoxidized phenol-aldehyde resin having an epoxy functionality greater than 2.

2. An epoxy resin according to Claim 1 wherein the polyol reactant is according to Formula I

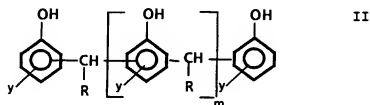


- wherein each A is independently -S-, -S-S-, -C(O)-, -S(O)-, -S(O)₂-, a divalent hydrocarbon radical containing from 1 to 8 carbon atoms or an oxygen, sulfur, or nitrogen containing hydrocarbon radical or a covalent bond; also A may be



each X is independently hydrogen, halogen, or an alkyl group containing from 1 to 4 carbon atoms, and n has an average value from greater than 0 to 5, preferably from 0 to 2; or Formula II

5

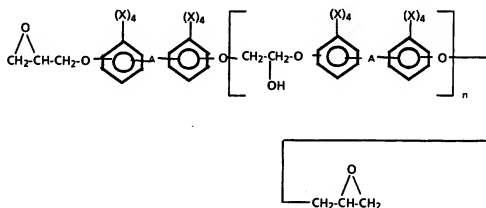


10 wherein each R is individually hydrogen or an alkyl radical having from 1 to 4 carbon atoms, each Y is independently hydrogen, chlorine, bromine or a lower alkyl group having from 1 to 4 carbon atoms and m has an average value from greater than 0 to 10 or mixtures of compositions of Formula I and II and an epoxy reactant according to Formula III

15

III

20



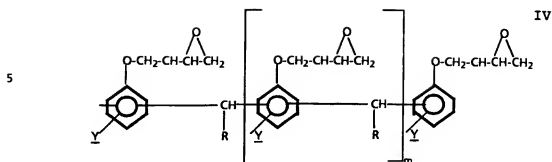
25

wherein each A and X are as described above in the description of Formula (I) and n has an average value of 0 to 4;

30

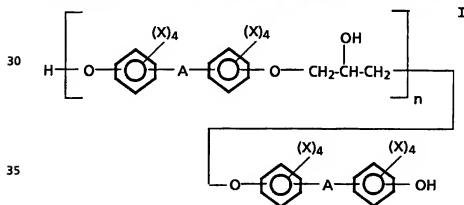
35

or Formula IV

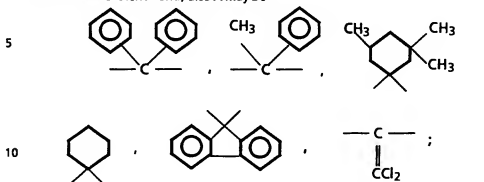


- 10 wherein R, Y and m are described as above with reference to Formula (II); polyglycidyl ethers of polyglycols such as the diglycidyl ether of polypropylene glycol, or the polyglycidyl ethers of tris(phenol)methane, or a triglycidyl ether of a triazine, for example triglycidyl isocyanurate, or a mixture of epoxy reactants such that the epoxy component and the hydroxy component are present in a ratio from 0.1:1 to 10:1, a reaction catalyst inhibiting the reaction progress at a
- 15 predetermined conversion of reactants at which point the resin has at least about 0.2 weight percent terminal hydroxyl end groups and at least about 0.2 weight percent epoxy end groups.

3. An epoxy resin according to Claim 2 wherein for components of Formula I, n has an average value from 0 to 2.
4. An epoxy resin according to Claim 2 wherein for components of Formula II m has an average value from 0 to 4.5.
5. An epoxy resin according to Claim 2 wherein for components of Formula III n has an average value from 0 to 2.
6. An epoxy resin according to Claim 2 wherein for reactants/components of Formula IV m has an average value from 0.5 to 4.5.
7. A method of making an epoxy resin composition comprising combining under isothermal reaction conditions a polyol reactant according to Formula I

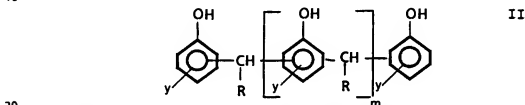


wherein each A is independently -S-, -S-S-, -C(O)-, -S(O)-, -S(O)₂-, a divalent hydrocarbon radical containing from 1 to 8 carbon atoms or an oxygen, sulfur, or nitrogen-containing hydrocarbon radical or a covalent bond; also A may be



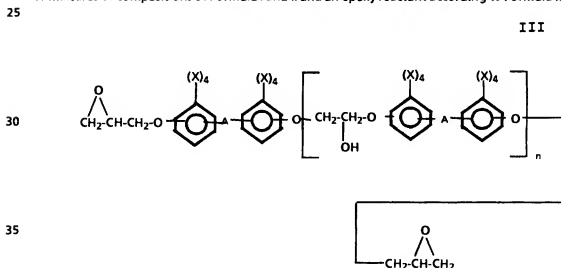
each X is independently hydrogen, halogen, or an alkyl group containing from 1 to 4 carbon atoms, and n has an average value of 0 to 5, preferably from 0 to 2;

or Formula II



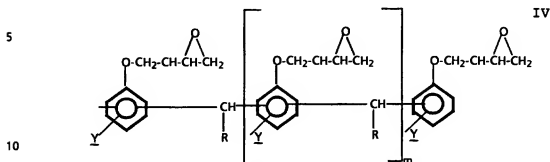
wherein each R is individually hydrogen or an alkyl radical having from 1 to 4 carbon atoms, each Y is independently hydrogen, chlorine, bromine or a lower alkyl group having from one to four carbon atoms and m has an average value from greater than 0 to 10,

or mixtures of compositions of Formula I and II and an epoxy reactant according to Formula III



wherein each A and X are as described above in the description of Formula (I) and n has an average value of 0 to 4;

or Formula IV



wherein R, Y and m are described as above with reference to Formula (II); polyglycidyl ethers of polyglycols such as the diglycidyl ether of polypropylene glycol, or the polyglycidyl ethers of tris(phenol)methane, or a triglycidyl ether of a triazine, for example triglycidyl isocyanurate, or a mixture of epoxy reactants such that the epoxy component and the hydroxy component are present in a ratio from 0.1:1 to 10:1, a reaction catalyst inhibiting the reaction progress at a predetermined conversion of reactants at which point the resin has at least about 0.2 weight percent terminal hydroxyl end groups and at least about 0.2 weight percent epoxy end groups.

8. The method of Claim 7 wherein for the components of Formula I n has an average value from 0 to 2.

9. The method of Claim 7 wherein for the components of Formula II m has an average value from 0.5 to 4.5.

10. The method of Claim 7 wherein for the components of Formula III n has an average value from 0 to 2.

11. The method of Claim 7 wherein for the reactants of Formula IV m has an average value from 0.5 to 4.5.

12. The method of Claim 7 wherein the mole ratio of epoxy component to phenolic hydroxyl component is from 0.3:1 to 5:1.

13. The method of Claim 7 wherein the reaction of the hydroxyl component and the epoxy component is catalyzed by a secondary tertiary amine, selected from the group consisting of benzyl dimethyl amine, triethyl amine and/or benzyl diethyl amine; the alkali metal hydroxides for example, potassium hydroxide; quaternary ammonium compounds such as tetralkylammonium tetraalkylammonium halides, for example, tetramethyl ammonium chloride and/or phosphines and/or quaternary phosphonium salts such as triphenyl phosphine and/or ethyl triphenyl phosphonium acetate.

14. The method of Claim 7 wherein the reaction mixture is maintained at an isothermal condition.

15. The method of Claim 7 wherein the epoxy-hydroxyl reaction is inhibited by the addition of a strong acid, the anhydride of a strong acid, or the ester of a strong acid.
16. The method of Claim 7 wherein the strong acid, anhydride or ester is phosphoric acid, phosphoric acid anhydride, dimethyl sulfate, alkyl and aryl sulfonic acids such as p-toluene acid, trichloroacetic acid; methyl-p-toluene sulfonate, ethyl-p-toluenesulfonate, and methane sulfonic acid methyl ester.
17. The method of Claim 7 wherein the epoxy-hydroxyl reaction is thermally inhibited by means of an extruder by increasing the temperature sufficiently to destroy the reaction catalyst, or by cooling the reactants sufficiently to effectively halt the reaction progress.
18. A heat-cured epoxy resin coating produced by curing at 90°C to 180°C within a 30 to 10 minutes cure time and possessing an impact resistance greater than 115 cm-kg forward, greater than 34.5 cm-kg reverse, an Erichsen Indentation greater than 6 mm, and Byk Flow greater than 2 when applied to steel panels.
19. A heat-cured epoxy resin coating according to Claim 18 cured at 90°C to 120°C within a 30 to 10 minutes cure time.

AMENDED CLAIMS

[received by the International Bureau on 27 December 1995(27.12.95);
original claim 18 amended; remaining claims unchanged (1 page)]

15. The method of Claim 7 wherein the epoxy-hydroxyl reaction is inhibited by the addition of a strong acid, the anhydride of a strong acid, or the ester of a strong acid.

16. The method of Claim 7 wherein the strong acid, anhydride or ester is phosphoric acid, phosphoric acid anhydride, dimethyl sulfate, alkyl and aryl sulfonic acids such as p-toluene acid, trichloroacetic acid; methyl-p-toluene sulfonate, ethyl-p-toluenesulfonate, and methane sulfonic acid methyl ester.

17. The method of Claim 7 wherein the epoxy-hydroxyl reaction is thermally inhibited by means of an extruder by increasing the temperature sufficiently to destroy the reaction catalyst, or by cooling the reactants sufficiently to effectively halt the reaction progress.

18. A heat-cured epoxy resin coating produced by curing at 90°C to 180°C within a 30 to 10 minutes cure time and possessing an impact resistance greater than 115 cm.kg forward, greater than 34.5 cm.kg reverse, an Erichsen Indentation greater than 6 mm, and Byk Flow greater than 2 when applied to DIN 1624 steel panels 1 mm thick.

19. A heat-cured epoxy resin coating according to Claim 18 cured at 90°C to 120°C within a 30 to 10 minutes cure time.

AMENDED SHEET (ARTICLE 19)

INTERNATIONAL SEARCH REPORT

International Application No.

PCT/US 95/01674

A. CLASSIFICATION OF SUBJECT MATTER
 IPC 6 C08G59/06 C08G59/38 C08G59/62

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
 IPC 6 C08G

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	WO,A,86 01216 (DOW CHEMICAL) 27 February 1986 see claim 1	7-16
Y	see page 10, line 15 - line 20 see page 12, line 27 - page 13, line 23 ---	1-6
Y	ML,A,6 717 669 (DOW CHEMICAL) 1 July 1969 see claim 1; examples 4-6 ---	1-6
X	WO,A,87 05036 (DOW CHEMICAL) 27 August 1987 cited in the application see examples 1-5 see page 9, line 30 - line 31 ---	1-16
X	EP,A,0 202 405 (DOW CHEMICAL) 26 November 1986 see claim 1 ---	7,17

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☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

* Special categories of cited documents:

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"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"A" document member of the same patent family

Date of the actual completion of the international search

9 October 1995

Date of mailing of the international search report

25. 10. 95

Name and mailing address of the ISA

European Patent Office, P.B. 5818 Patentaan 2
 NL - 2200 HV Rijswijk
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 Fax (+ 31-70) 340-3016

Authorized officer

O'Sullivan, T

INTERNATIONAL SEARCH REPORT

Int. l. Application No.

PCT/US 95/01674

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US,A,3 367 990 (BREMNER B.J.) 6 February 1968 see claim 1 -----	1-19
A	EP,A,0 493 916 (CIBA-GEIGY) 8 July 1992 see claim 1 -----	1-19

INTERNATIONAL SEARCH REPORT

International Application No

PCT/US 95/01674

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		FI-B- 89376	15-06-93
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		JP-T- 62502621	08-10-87
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		SG-A- 32494	28-10-94
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Organic Chemistry

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ORGANIC CHEMISTRY

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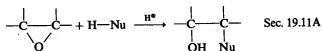
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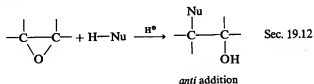
19.23 Summary of Reactions of Epoxides

A. Ring Opening by Acidic Reagents

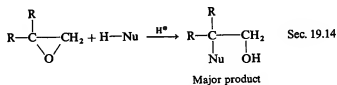
General:



Stereochemistry:

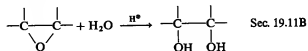
With H_2O , *anti*-hydroxylation occurs.

Orientation:

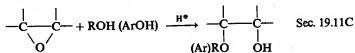


Nucleophile ends up on more highly substituted carbon.

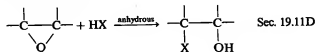
1. Reaction with water



2. Reaction with alcohol or phenol

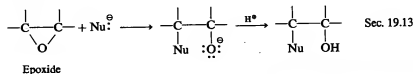


3. Reaction with hydrohalic acid

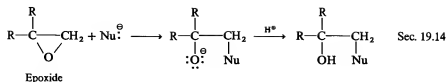


B. Ring Opening by Basic Reagents

General:

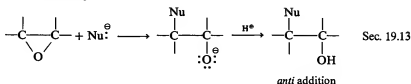


Orientation:

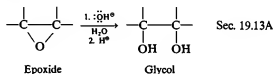


Nucleophile ends up on less highly substituted carbon.

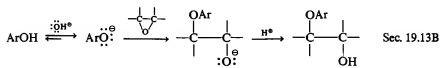
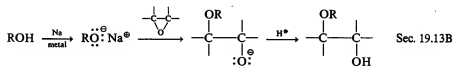
Stereochemistry:



1. Reaction with water



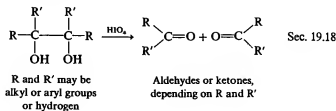
2. Reaction with alcohol or phenol



19.24 Summary of Reactions of Glycols

(Note: A summary of the methods of preparing glycols is given in Sec. 19.17.)

Oxidation by periodic acid:



Study Questions

19.28 Draw and name all the isomeric compounds that contain an aromatic ring and have the molecular formula $\text{C}_7\text{H}_8\text{O}$.19.29 Draw and name all the isomeric ethers that have the molecular formula $\text{C}_4\text{H}_{10}\text{O}$.